

Polar ferrocene phosphinoamides

Polar phosphane-carboxamides 1-(diphenylphosphanyl)-1'-[N-(2-hydroxyethyl)carbamoyl]ferrocene (**4**) and 1-(diphenylphosphanyl)-1'-[N,N-bis(2-hydroxyethyl)carbamoyl]ferrocene (**5**) bearing hydroxyethyl pendants derived from 1'-(diphenylphosphanyl)-1-ferrocene-carboxylic acid (Hdpf) were synthesized either by direct amidation or via active pentafluorophenyl ester (**3**). Reactions of **4** and **5** with [PdCl₂(cod)] (cod = $\eta^2:\eta^2$ -cycloocta-1,5-diene) afforded the respective bis(phosphane) complexes *trans*-[PdCl₂L₂] (**6**, L = **4**; **7**, L = **5**). Depending on the solvent used in their subsequent crystallisation (ethanol or chloroform), the complexes were isolated as distinct solvatomorphs. All new compounds have been characterised by spectral methods and by X-ray crystallography. The structure determination for both ligands and solvated complexes (**6**·2EtOH, **6**·6CHCl₃, **7**·2EtOH, and **7**·4CHCl₃) revealed the dominating role of hydrogen bond interactions in their solid-state assemblies. The nature and complexity of the hydrogen bonded arrays changed broadly along with the ligand structure (one vs. two 2-hydroxy-ethyl chains) and their number in the discrete species (free ligand vs. the complexes), and also with the solvent properties. Catalytic tests performed with **6** and **7** on Suzuki-Miyaura cross-coupling reaction showed that both complexes form active catalysts for the coupling of aryl bromides with phenylboronic acid in polar reaction media including water and toluene-water biphasic mixture. Comparison of the catalytic results indicates that **6** gives rise to a more active and stable catalyst, which can be reused five times without any detectable loss of activity in toluene/water biphasic system.